

PLASMA REFORMER FOR HYDROGEN PRODUCTION FROM WATER AND FUEL

BACKGROUND OF THE INVENTION

[0001] This invention pertains to a plasma reformer for dissociating H₂O and hydrocarbon fuels to produce hydrogen for direct use or for use in a fuel cell and carbon oxides. More particularly it pertains to dissociating H₂O into hydrogen and oxygen in a plasma reformer that uses a hydrocarbon fuel as an initiator and an intense electron field under non-equilibrium thermal plasma conditions to dissociate H₂O.

[0002] Hydrogen powered fuel cells have long been recognized as having great potential for stationary power generation and for transportation applications. Advantages of fuel cells include their ability to generate power more efficiently than internal combustion engines and other conventional power sources while producing essentially no pollutants. However, currently, no scalable, cost-effective, environmentally attractive hydrogen production process is available for commercialization. Hydrogen can be produced from dissociation of H₂O or from reforming of hydrogen fuels. Dissociation of H₂O is ideal from an environmental perspective because it produces no greenhouse gases; however, dissociation of H₂O through electrolysis is energy-intensive and prohibitively expensive.

[0003] Hydrogen can be produced from hydrocarbon fuels with use of conventional technologies such as steam reforming, partial oxidation, and auto-thermal reforming. For example, Takahashi in U.S. Patent No. 5,746,985 and Edlund, et al in U.S. Patent No. 6,221,117 teach use of steam reforming reactions; Krumpelts, et al in U.S. Patent No. 5,942,346 and Ahmed, et al in U.S. Patent Nos. 5,939,025 teach use of partial oxidation reactions. However, these technologies tend to require large components and to be not efficient in meeting large demands, a disadvantage for space-limited facilities such as fueling stations. There are also several technical issues such as capability for fast starts, fast response to load changes, sulfur contamination, and soot or carbon formation. One problem common to conventional reforming is sulfur removal. Conventional reformer technology requires removal of sulfur from liquid fuels, which is usually accomplished with use of

catalysts and heavy heaters. Such components usually raise gas poisoning and temperature sensitivity issues. Also in conventional reformer technology, poor fuel dispersion will create uneven fuel distribution and result in carbon/coke formation in fuel-rich zones and hot spots in fuel-lean zones.

[0004] The inventor has developed technology for dissociating compounds in a thermoelectric reactor using ultra-pyrolysis techniques with thermal radiation enhancement, non-equilibrium reactions derived from electromagnetic forces, and energy trapping to achieve and maintain temperatures sufficient to achieve very high conversion rates. When the compound contains hydrogen, such as hydrocarbon fuels and hydrogen sulfide, its dissociation produces hydrogen. The inventor has taught the use of thermoelectric reactors to destroy volatile organic compounds in U.S. Patent No. 5,614,156, to dissociate hydrogen sulfide into hydrogen and sulfur in U.S. Patent No. 5,843,395, and to reform hydrocarbon fuels to produce hydrogen in co-pending U.S. Application Serial No. 10/121,390.

[0005] Such a reactor has recently been tested for reforming several transportation fuels to produce hydrogen. The results are given in Table 1.

[0006] Table 1.

Fuel	Electricity Consumption ¹ , %	Fuel Conv. Eff. ² , %	H ₂ Conv Eff. ³ , %	Energy Eff. ⁴ , %	H ₂ Conc. ⁵ (dry) %
Methanol	<3	~100	93-95	~100	64
Ethanol	<6	~100	94	~100	54
Gasoline	<6	~100	97	~100	65

Note: ¹ Electric power input = % of power output (H₂)

² Fuel Conversion Efficiency = 1 - (fuel in reformat)/(input fuel)

³ H₂ Conversion Efficiency = (H₂ measured in reformat)/(H₂ theoretical value in equilibrium)

⁴ Energy Efficiency = (LHV of H₂ in reformat)/(LHV of input fuel + electric power input)

⁵ Measured H₂ concentration in reformat as dry basis. This concentration was measured right after the H₂ reformer (without any other gas conditioning).

LHV = Low Heating Value

1 [0007] The U.S. Department of Energy (USDOE)¹ estimates that currently it costs
2 between \$5.00 and \$6.00 to produce a kilogram of hydrogen, and that this cost should be
3 reduced to \$1.50/kg to be competitive with conventional fuels. The USDOE has also set a
4 primary energy efficiency of 75% to be met in the year 2010. The primary energy
5 efficiency of conventional reformer technology for producing hydrogen currently ranges up
6 to 70%. Thus a three to four-fold decrease in cost is necessary for hydrogen to become a
7 competitively priced fuel. A significant fraction of the cost of hydrogen production is the
8 cost of the hydrocarbon fuels that are reformed. If H₂O were to replace hydrocarbon fuels
9 as the primary source of hydrogen in a reformer, such cost reductions are feasible.

10 [0008] It is difficult to dissociate H₂O with thermal energy because very high
11 temperatures, in excess of 2500°C, are needed. Also, it is difficult to ionize H₂O because it
12 has a higher ionization energy potential and enthalpy formations of ions (12.6 eV and 976
13 kJ/mol, respectively) than hydrocarbon fuels of interest. For example, gasoline has an
14 ionization energy of 9.8 eV and an enthalpy formation of ions of 737 kJ/mol. In addition, it
15 is difficult to ionize H₂O using high energy (“hard”) electrons because H₂O is a small
16 molecule that has a small bombardment target area for ionization by high energy (hard)
17 electrons that are newly emitted from electrodes. However, H₂O much more readily absorbs
18 low energy (“soft”) electrons that have lost much of their energy in collisions with other
19 ions and hydrocarbon molecules. Thus hydrogen can be produced in a reformer from
20 dissociation of H₂O through ionization and from dissociation of hydrocarbon fuels through
21 heat and ionization when the temperature in the reaction chamber of reformer is sufficiently
22 high (in excess of 700°C) and when there is an intense field of low energy electrons. These
23 conditions can be created or found in some plasmas.

24 25 SUMMARY OF THE INVENTION

26 [0009] The present invention is a reformer that dissociates a gaseous
27 H₂O/hydrocarbon fuel input mixture in a non-equilibrium thermal plasma environment. The
28 heart of the reformer is a reaction chamber. The outer lateral wall of the reactor is an
29 emitter electrode and the inner lateral wall is a collector electrode, the emitter electrode and

1 the collector electrode forming an electric circuit. The emitter electrode contains a
2 multiplicity of thin needle-like extrusions. External electricity causes electrons to be
3 emitted copiously from the needle-like extrusions. Spindt² discusses how these could be
4 produced. These high energy electrons are absorbed by hydrocarbon molecules and ionize
5 the hydrocarbon molecules to create a greater number of lower energy electrons than were
6 absorbed. These lower energy electrons in turn interact with H₂O to dissociate it. A non-
7 combustion pyrolysis process is used to create and maintain this environment. Dissociation
8 of H₂O is induced by ionization in the plasma environment. The present invention in part
9 replaces hydrocarbon fuels, which have costs, with H₂O, which is virtually without cost, as a
10 fuel for producing hydrogen. Preliminary cost estimates based on H₂O replacing 50% of the
11 hydrocarbon fuel and a nearly 100% primary energy efficiency indicate that a cost of less
12 than \$2.00/kg of hydrogen can be achieved. This cost can be further reduced through
13 optimization of the system and operational conditions so that the cost target of \$1.50/kg of
14 hydrogen is feasible. Therefore, an object of the invention is to reduce the cost of producing
15 hydrogen to commercially competitive levels while reducing the consumption of
16 hydrocarbon fuels. Other objects that result from reduced use of hydrocarbon fuels are
17 reducing the production of greenhouse gases and if the hydrocarbon fuels are fossil fuels,
18 reducing the use of scarce or imported fuels.

19 [0010] Reforming techniques that use combustion require introduction of air. The
20 introduction of air causes nitrogen dilution, increases product gas volume, causes polluting
21 nitrogen oxides emissions, and causes formation of free oxygen, which compromises
22 hydrogen safety. Therefore, another object of the invention is to eliminate the undesirable
23 consequences of using combustion. The external supplemental energy source for the
24 invention is electricity. This allows for quick starts and quick response to transient load
25 changes, and provides control for maintaining optimum conditions for hydrogen production.
26 Therefore, another object of the invention is to provide a quick-starting/responding and
27 readily controlled reformer for producing hydrogen.

28 [0011] Reforming techniques that use catalysts require large reaction areas. This
29 large-area requirement imposes scalability problems and limits the quantity of hydrogen that

1 can be produced at locations with limited space such as refueling stations in a city. Since
2 this invention does not use catalysts, another object is to provide a scalable and high-power
3 density reformer for hydrogen production. The presence of H₂O results causes chemical
4 reactions wherein carbon dioxide rather than carbon or soot is formed. Therefore another
5 object of the invention is to avoid carbon or soot formation.

7 BRIEF DESCRIPTION OF THE SEVERAL VIEWS

8 [0012] FIG. 1 shows an elevational cross section of the plasma reformer.

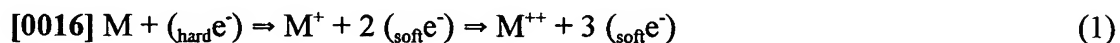
9 [0013] FIG. 2 is a graph of ionization potential of various hydrocarbons as a
10 function of carbon number

11 [0014] FIG. 3 is a graph of molar water to hydrocarbon fuel ratio as a function of
12 carbon number.

14 DETAILED DESCRIPTION OF THE INVENTION

15 [0015] With reference to FIG. 1 the plasma reformer, has an inlet 33 to admit a flow
16 of a gaseous mixture of H₂O and hydrocarbon fuel into the plasma reformer. This mixture
17 is preheated to a temperature in the range of 350°C to 500°C external to the reformer and
18 then further heated and mixed in turbulent heating zone 35. The mixture then enters
19 reaction chamber 45. The reaction chamber contains emitter electrodes 10 and collector
20 electrodes 20. These electrodes form an electric circuit and are at high temperature being
21 heated by an external supplemental source of electricity. The electrical energy produces
22 active energetic electrons ($_{\text{hard}}e^-$), and maintains and controls optimal plasma conditions.
23 These hard electrons produce excited species ions, free radicals, and additional lower energy
24 electrons ($_{\text{soft}}e^-$) through electron-impaction or electron-expelling dissociation, excitation,
25 and ionization of hydrocarbon molecules. There could be a single emitter electrode or
26 multiple emitter electrodes. When multiple electrodes are used there could be in circuits
27 using different external sources of electricity, such as 110 volt AC, 220 volt AC or DC. The
28 emitter electrode(s) 10 are embedded in, the outer lateral walls of the reaction chamber.
29 The collector electrode(s) 20, which can be single or multiple, form or are embedded in the

inner lateral wall of the reaction chamber. It is preferred that a filter 15, which could be made of a semiconductor, such as silicon-based zirconium oxide, or a ceramic alloy such as alumina surrounds the collector electrode(s). The filter acts to neutralize ions and to allow passing of electrons to the collector electrode(s) while slowing them down so that they impart less kinetic energy (heat) to the collector electrode(s).. The filter also acts as a thermal radiation shield to cool the collector electrode(s) to improve their effectiveness. The hot emitter electrode(s) emit active high-energy electrons ($_{\text{hard}}e^-$) that may be absorbed by hydrocarbon molecules in the reaction chamber or may expel orbital electrons from the hydrocarbon molecules if the energy transferred to the molecule exceeds the ionization potential of the molecule. When an orbital electron is expelled, the molecule becomes ionized and the incident or expelled electron loses energy and becomes a lower energy or soft electron ($_{\text{soft}}e^-$). The energy-degraded incident electron and the expelled electrons are soft electrons. More than one orbital electron can be expelled as shown in Eq. 1, where M represents a molecule:



[0017] H_2O has a high ionization potential $(12.6\text{eV})^2$ and is a small molecule that presents a small target for hard electrons. Hydrocarbons are larger molecules and those that have a lower ionization potential than water are more readily ionized by hard electrons. FIG. 2 shows that the ionization potential of hydrocarbon decreases as the number of carbon atoms in the molecule, the carbon number, increases³. Ionization originates with ionization of hydrocarbons near the surface of the emitter electrodes 10. These red-hot electrodes also originate an electricity-conducting gas medium that propagates from the emitter electrodes to the collector electrodes 20. The hydrocarbon fuel in addition to being dissociated itself, by being initially ionized initiates plasma conditions that have a field of soft electrons. The soft electrons thus produced readily interact with and are absorbed by the superheated H_2O steam molecules that are energetic at the high temperatures in the reaction chamber. Soft electrons with energies about 5 eV to 6 eV are optimum for dissociating H_2O , into hydrogen

and oxygen through electron impaction or absorption. Hard electrons with energy above 7 eV and ions play key roles in dissociating and ionizing hydrocarbon fuels. For hydrogen production, the preferred temperature range in the chamber is 700°C to 1000°C, although the temperature could range from 400°C upwards to 1900°C. As shown in Eq. 2, steam interacts with soft electrons to form ionized H₂O, or hydro-radicals, which dissociates into hydrogen and oxygen. The oxygen thus produced reacts with carbon from dissociation of the hydrocarbon fuel to form carbon oxides, CO_x, instead of forming carbon or coke.



[0019] FIG. 3 plots the molar ratio of H₂O to hydrocarbon fuel to obtain reactions as a function of carbon number. The figure shows that the H₂O/fuel ratio is a linear function of carbon number. The greater the carbon number of the hydrocarbon fuel, the greater is the percentage of hydrogen that is produced from dissociation of H₂O. The solid line (MR) was obtained from preliminary demonstration tests performed by the inventor in which the ratio of H₂O/fuel was arbitrarily limited. The dotted line (SR) represents the theoretical stoichiometric ratio, the ratio for which all the oxygen from the dissociated H₂O reacts with all the carbon from the dissociated hydrocarbon fuel to form carbon dioxide. With careful selection of electrode material, and optimized reaction chamber design and operational conditions, the value of H₂O/fuel molar ratio can approach and possibly slightly exceed the stoichiometric ratio. This means that the majority of hydrogen produced by this reformer can be produced from H₂O, with hydrocarbon fuel acting as only an initiator, agent, or promoter.

[0020] There are no chemical catalysts, such as nickel or platinum in the reaction chamber. However, the chamber internals (walls, electrodes, filter, and other solid structures) are activated by active, highly energetic electrons and ions so they will act as catalysts. Therefore, the temperature range where plasma reactions occur is lowered to 700°C to 1,000°C.

1 **[0021]** For the plasma reformer to perform well, the emitter electrodes should be
2 made of a suitable emitter material. Emitter electrodes should be capable of (1) supplying
3 heat to maintain high temperatures in the reaction chamber of the plasma reformer; and (2)
4 emitting electrons from their surfaces. The properties of good emitter materials are: (1) a
5 high electron emission capability; (2) low rate of deterioration; (3) low emissivity to reduce
6 thermal radiation of the emitters; and (4) no reactions with the hydrocarbon fuel and the
7 surrounding walls, including the filter and collector electrodes. Materials that have these
8 properties include chromium, niobium, tungsten, titanium, zirconium, molybdenum, and
9 other transition metals of the Periodic Table. The collector electrode material should have a
10 low work function. The lower the work function, the less energy electrons give up entering
11 the collector surface. Preferred emitter and collector materials are tungsten, zirconium,
12 titanium, molybdenum, or alloys thereof. The number, shape, and orientation of electrodes
13 are also important. It is preferred that emitter electrode surfaces have needle-type
14 extrusions (with a diameter from 1-2 nanometers to 100 micrometers) to enhance electron
15 emission. Such needle-type extrusions can be grown with special design and treatment,
16 such as acidic etching and chemical vapor deposition. A high electron emission rate will
17 result in a high population of electrons in the reaction chamber and will increase the
18 probability of ionization of the hydrocarbon fuel and dissociation of H₂O.

19 **[0022]** To maintain the high temperature range that is required in reaction chamber
20 **45**, the plasma reformer should surround it with layers of insulation. A preferred
21 embodiment, as shown in FIG. 1 should have the following structure. Proceeding from the
22 outside of the reformer inward there is steel casing **31**, compression-expansion cushion mat
23 **40**, insulating high-temperature fiber blankets **30**, high temperature vacuum form fibers **29**,
24 a ceramic outer wall **28**, an energy retaining zone **27**, a ceramic inner wall **26**, and turbulent
25 heating zone **35** and reaction chamber **45**. The emitter electrodes **10** are on the inner surface
26 of the inner wall. Vacuum form fibers are formed with higher density and a higher
27 percentage of higher melting/boiling point ceramic materials than fiber blankets.

28 **[0023]** The high-temperature fiber blankets **30** and vacuum form fibers **29** are
29 typically ceramic fibers, which may be composed of commercially-available alumina, silica,

1 or mullite. These materials have very low thermal conductivities (of the order of 0.04
2 watts/meter- °C) and are capable of withstanding high temperature (up to at least 1900 °C).
3 The compression-expansion cushion mat **40** provides thermal expansion cushion as well as
4 cushioning for vibration and shocks; seals the contact between the reformer's outer steel
5 casing **31** and the internals including the insulators **29** and **30**, and the ceramic outer wall
6 **28**; provides thermal insulation; and maintains the system durability throughout the life
7 cycle of the reformer. The compression-expansion mat **40** is made of a low thermal
8 conductivity material that has a great capability for absorbing thermal compression-
9 expansion, shocks, and vibrations, and having the capability of sealing and protecting
10 reformer internals. A commercially available mat product consisting of three basic raw
11 material (ceramic fibers, unexpanded vermiculite, and organic binder) is an appropriate
12 material for the compression-expansion mat. The ceramic walls **26** and **28** may be
13 zirconium oxide, silicon carbide or graphite. The energy retaining zone **27** and turbulent
14 heating zone **35** contain layers of heat-retaining micro-porous articulated ceramic fibers,
15 such as alumina, silica, mullite, titanate, spinel, zirconia, or some combination thereof. The
16 physical properties of these ceramic fibers (such as thermal emissivity, absorptivity,
17 reflectivity, conductivity, porosity) have some impact on energy efficiency and may
18 increase or decrease energy efficiency by as much as approximately 10 percent. The choice
19 of ceramic fibers can be optimized for specific feed streams by considering the conductive,
20 convective, and radiative heat transfer in a porous medium reactive flow for different types
21 of ceramic fibers.

22 **[0024]** A gaseous or vaporized feed stream enters the reactor chamber by means of
23 inlet **33** that penetrate the bottom of the reactor's steel casing **31**, compression-expansion
24 cushion mat **40**, insulating high-temperature fiber blankets **30**, high-temperature vacuum
25 form fibers **29**, and ceramic inner wall **26**. The feed stream enters the turbulent heating
26 zone **35** where it is subject to turbulent mixing and is rapidly heated by conduction,
27 convection, and radiation. Within the reaction chamber **45**, the gaseous H₂O and
28 hydrocarbon fuel stream is heated further by radiation to temperatures sufficient to reform

1 the chemical bonds of the hydrocarbon fuel, and the H₂O and hydrocarbon fuel are
2 dissociated through ionization as described previously.

3 **[0025]** After leaving the reaction chamber, the reformat stream passes through the
4 energy retaining zone **27**, where further thermal reforming continues to occur, and exits the
5 reactor through outlet **32**. Reforming in the energy retaining zone helps to complete the
6 reforming of the chemical compounds in the feed stream. Electrons or ions that escape from
7 the reaction zone and flow downstream are also neutralized by direct impact within high-
8 contact areas and micro-porous structure in the heat-retaining zone. The unique design of
9 the energy-retaining zone (downstream of the reaction chamber) and the turbulent-heating
10 zone underneath (or upstream of) the reaction chamber is attributable to the use of micro-
11 porous structure technology. The advantages of this micro-porous structure design include
12 (1) the creation of a rapid mixing and heating environment; (2) the promotion of excellent
13 heat and mass transfer; (3) the creation of thermal uniformity for reforming uniform
14 products; (4) the trapping of most heat energy within the turbulent-heating and energy-
15 retaining zones; and (5) the maintaining of extremely high temperature in the reaction
16 chamber. These advantages significantly reduce the cold-start and transient response times
17 from transient load change of the feed stream. There are two sources of energy in the
18 plasma reformer, electrical energy and chemical energy from the input fuel. The electrical
19 energy initiates ionization that leads to release of the chemical energy. The electrical
20 energy, which controls maintaining optimal plasma conditions at a pre-set temperature,
21 serves as a supplement to the chemical energy released. The electrical energy is nearly
22 independent of the amount of chemical energy released but is much smaller than the amount
23 of chemical energy. This electrical ionization (or plasma) amplified with large chemical
24 energy release from the fuel initiates the gas-phase electrolysis, or plasma-induced steam
25 reforming that produces additional hydrogen from the water.

26 **[0026]** Inlet **33** and outlet **32** preferably have double walls tubes to prevent leaks.
27 These double-walled tubes have an inner wall of a ceramic material that can withstand high
28 temperatures and contact with a potentially corrosive feed, or product stream, and an outer
29 wall of stainless steel that can withstand high temperatures.